BASE MATERIAL FOR LAMINATED SHEET, PREPREG AND PRODUCTION THEREOF

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Abstract of **JP2000334871**

PROBLEM TO BE SOLVED: To provide a base material for a laminated sheet excellent in characteristics and capable of being treated under heating and pressure at sufficiently high temp.
SOLUTION: A base material for a laminated sheet has a multilayered structure having at least three layers, that is, both outer layers and an inner layer and the inner layer (1) is a nonwoven fabric containing synthetic org. fibers with a softening temp. of 320 deg.C or lower and a moisture absorbing ratio of 1.5% or less and both outer layers (2) comprise a nonwoven fabric which contains 70% or more of synthetic org. fibers having no m.p. and a decomposition temp. of 400 deg.C or higher and of which the content of synthetic org. fibers with a softening temp. of 320 deg.C or lower is less than that of the inner layer.

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(54) [Title of Invention]: SUBSTRATE FOR LAMINATED SHEET, PREPREG, AND PROCESS FOR MANUFACTURE THEREOF

(57) [Abstract]

[Problem]

To provide a substrate for laminated sheets having excellent characteristics as a substrate for laminated sheet, which permits a treatment with heat and pressure at a sufficiently high temperature.

[Means Used to Solve the Problem]

A substrate for a laminated sheet with a multi-layer structure comprising at least 3 layers, wherein both exterior layers and an interior layer(s) have the following construction:

(1) the interior layer is constituted of a non-woven fabric containing a synthetic organic fiber having a softening temperature of not higher than 320°C and a moisture absorption of not more than 1.5%; and

(2) both exterior layers are constituted of a non-woven fabric containing at least 70% of a synthetic organic fiber having no melting point but having a decomposition temperature of at least 400°C, in which the content of synthetic organic fiber having a softening temperature not higher than 320°C is less than that in the interior layer.

[CLAIMS]

[Claim 1]

A substrate for a laminated sheet with a multi-layer structure comprising at least 3 layers, wherein both exterior layers and an interior layer(s) have the following construction:

(1) the interior layer is constituted of a non-woven fabric containing a synthetic organic fiber having a softening temperature of not higher than 320°C and a moisture absorption of not more than 1.5%; and

(2) both exterior layers are constituted of a non-woven fabric containing at least 70% of a synthetic organic fiber having no melting point but having a decomposition temperature of at least 400°C, in which the content of synthetic organic fiber having a softening temperature not higher than 320°C is less than that in the interior layer.

[Claim 2]

A substrate for a laminated sheet as set forth in Claim 1, wherein the synthetic organic fiber in the interior layer having a softening temperature of not more than 320°C and a moisture absorption of not more than 1.5% is at least one fiber selected from the group consisting of polyarylate fibers, polyphenylene sulfide fibers, and fluororesin fibers.

[Claim 3]

A substrate for a laminated sheet as set forth in Claim 1 or Claim 2, wherein the synthetic organic fiber in the interior layer having a softening temperature of not higher than 320°C and a moisture absorption of not higher than 1.5% is present in the interior layer in an amount of not less than 30%.

[Claim 4]

A substrate for a laminated sheet as set forth in any one of the Claims 1-3, wherein the synthetic organic fiber of both exterior layers having no melting point but having a decomposition temperature of at least 400°C is at least one fiber selected from the group consisting of p-phenylene terephthalamide fibers, p-phenylene diphenyl ether terephthalamide fibers, poly-p-phenylene benzbisoxazole (PBO) fibers.

[Claim 5]

A process for the manufacture of a substrate for a laminated sheet having a multi-layer structure comprising at least 3 layers, which comprises the steps of

individually papermaking non-woven fabrics having constructions given below, by a wet papermaking process;

overlaying one on top of the other; and

bonding them together by carrying out a treatment with heat and pressure using hot rolls at a surface temperature of 280°C-450°C; wherein

(1) the non-woven fabric for the interior layer is a non-woven fabric containing a synthetic organic fiber having a softening temperature not higher than 320°C and a moisture absorption not higher than 1.5%;

(2) the non-woven fabric for both exterior layers is a non-woven fabric containing at least 70% of a synthetic organic fiber having no melting point, but having a decomposition temperature of at least 400°C and having a content of synthetic organic fiber having a softening temperature not higher than 320°C and a moisture absorption not higher than 1.5% at less than that in the interior layer.

[Claim 6]

A prepreg prepared using a substrate for a laminated sheet as set forth in any one of the Claims 1-4.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Utility]

The present invention relates to a substrate for laminated sheet which is used in printed wiring boards.

[0002]

[Prior Art]

With advancing miniaturization and higher functionalization of electronics in the recent years, printed wiring boards are also moving toward higher density wiring, and the parts being mounted are being shifted from an insertion system [Through hole technology] to a surface mount system, with the method of mounting also being shifted into a surface mount method as the major system. In such a system, connection reliability between parts such as

the chips being surface mounted and the printed wiring board is a critical problem. It is necessary to bring the coefficients of thermal expansion of the two to be as close as possible. The recent thin surface mount type chip has a thermal coefficient of expansion of 5 x 10^{-6}/°C, while a baseboard made of a glass non-woven fabric impregnated with an epoxy resin has a thermal coefficient of expansion about 3 times that of the chip.

[0003]

In addition, the delay time in signal propagation within a printed wiring board turns out to be very important, [the improvement of] which requires a low dielectric constant substrate for the laminated sheet. In general, a conventional FR-4 has a dielectric constant of about 4.7-5.1, and such a relatively high dielectric constant retards the propagation speed of an electrical pulse between the adjacent signal circuits, resulting in an excessive signal delay time. Incidentally, FR-4 is a copper-clad laminated sheet for a printed wiring board obtained by lamination of an epoxy resin-impregnated glass fabric substrate. (JIS Specification NEMA number)

[0004]

The above requirements have led to studies of laminated sheets, a basic material for printed wiring boards, using a laminated sheet obtained from a synthetic organic fiber non-woven fabric impregnated with an epoxy resin or the like. For example, under consideration is a laminated sheet based on a non-woven fabric substrate made of a para-aramid fiber having a negative thermal coefficient of expansion and having a low dielectric constant.

[0005]

There are a number of fibers considered to be excellent for applications in laminated sheets in terms of moisture absorption, dielectric constant, and the like, including for example, polyarylate fibers, fluorofibers, PPS fibers and the like. For example, Japanese Patent Application Publication Kokai 10-37054 discloses substrate for a laminated sheet comprising an all-aromatic polyamide, polyparaphenylene benzobisoxazole (PBO), all-aromatic polyester, polyphenylene oxide (PPO), polyphenylene sulfide, (PPS), fluororesin, and the like.

[0006]

As described above, formulation of a variety of organic fibers permits manufacture of laminated sheets having excellent properties not seen in conventional baseboards in terms of the coefficient of thermal expansion, moisture absorption, dielectric constant, and the like. While low moisture absorption and low dielectric constant are useful properties among characteristics of substrates for laminated sheets, nearly all fibers having such characteristics at present soften with heat. Formulating with a large amount of such a fiber will present the following problems:

[0007]

A substrate for laminated sheets mainly comprised of a synthetic organic fiber in general requires a density adjustment to reach an appropriate amount of varnish resin impregnation, and it also receives a treatment with heat and pressure by hot rolls. These substrates tend to warp with heat from solder reflow, so that in order to minimize such warpage, it is preferred to provide these substrates with a treatment at a temperature higher than the solder reflow equivalent temperature, at least in terms of warpage. However, substrates with increased content of a fiber which softens with heat have tended to suffer from the fiber melt-sticking to the tool used for a treatment with heat and pressure such as a hot calender or the like, with the resultant tool dirtying considerably reducing production efficiency, or in some cases, has made manufacture impossible to carry out. Also there have been cases where one was forced into using a lower temperature treatment in order to avoid any dirtying of the tools used for treatment with heat and pressure, resulting in a substrate for laminated sheets having too low a density or having substantial warpage in the laminated sheet.

[0008]

[Problem to be Solved by the Invention]

It is an object of the present invention to provide a substrate for laminated sheet and a prepreg which permit the production of low moisture absorption laminated sheets. It is also a further object to provide a substrate for laminated sheets that will not cause any dirtying of tools such as hot rolls, thereby permitting a treatment with heat and pressure at sufficiently high temperature, and further to provide a process for the manufacture thereof. It is a further object of this invention to provide a

substrate for laminated sheets having excellent characteristics such as a low dielectric constant and low warpage and the like.

[0009]

[Means Used to Solve the Problem]

The present inventors conceptualized a substrate for laminated sheets of a multi-layered structure having 3 layers or more. This substrate is characterized in that layers having different physical properties can be formulated for the two exterior layers and for the interior layer, thereby providing a substrate for laminated sheets having the [best] characteristics of each of the respective layers. That is, the invention enables one to formulate a large amount of a fiber which has excellent properties as a substrate for laminated sheets but which tends to soften with heat for the interior layer, and to formulate a fiber which is highly heat resistant and resistant to tool dirtying for the two exterior layers which come in contact with the tools used for treatment with heat and pressure. This can provide a substrate for laminated sheets which exhibits excellent properties and yet will not cause any tool dirtying even when subjected to a high temperature treatment with heat and pressure. The makeup of this invention is as follows:

[0010]

Invention 1 of the present invention is a substrate for a laminated sheet with a multi-layer structure comprising at least 3 layers, wherein both exterior layers and an interior layer(s) have the following construction:

(1) the interior layer is constituted of a non-woven fabric containing a synthetic organic fiber having a softening temperature of not higher than 320°C and a moisture absorption of not more than 1.5%; and

(2) both exterior layers are constituted of a non-woven fabric containing at least 70% of a synthetic organic fiber having no melting point but having a decomposition temperature of at least 400°C, in which the content of synthetic organic fiber having a softening temperature not higher than 320°C is less than that in the interior layer. Invention 2 of the present invention is a substrate for a laminated sheet as set forth in Invention 1, wherein the synthetic organic fiber in the interior layer having a softening temperature of not more than 320°C and a moisture absorption of not more than

1.5% is at least one fiber selected from the group consisting of polyarylate fibers, polyphenylene sulfide fibers, and fluororesin fibers.

[0011]

Invention 3 of the present invention is a substrate for a laminated sheet as set forth in Invention 1 or 2, wherein the synthetic organic fiber in the interior layer having a softening temperature of not higher than 320°C and a moisture absorption of not higher than 1.5% is present in the interior layer in an amount of not less than 30%. Invention 4 of the present invention is a substrate for a laminated sheet as set forth in any one of the Inventions 1-3, wherein the synthetic organic fiber of both exterior layers having no melting point but having a decomposition temperature of at least 400°C is at least one fiber selected from the group consisting of p-phenylene terephthalamide fibers, p-phenylene diphenyl ether terephthalamide fibers, poly-p-phenylene benzbisoxazole (PBO) fibers.

[0012]

Invention 5 of the present invention is a process for the manufacture of a substrate for a laminated sheet having a multi-layer structure comprising at least 3 layers, which comprises the steps of

individually papermaking non-woven fabrics having constructions given below, by a wet papermaking process;

overlaying one on top of the other; and

bonding them together by carrying out a treatment with heat and pressure using hot rolls at a surface temperature of 280°C-450°C; wherein

(1) the non-woven fabric for the interior layer is a non-woven fabric containing a synthetic organic fiber having a softening temperature not higher than 320°C and a moisture absorption not higher than 1.5%;

(2) the non-woven fabric for both exterior layers is a non-woven fabric containing at least 70% of a synthetic organic fiber having no melting point, but having a decomposition temperature of at least 400°C and having a content of synthetic organic fiber having a softening temperature not higher than 320°C and a moisture absorption not higher than 1.5% at less than that in the interior layer. Invention 6 of the present invention is a prepreg prepared using a substrate for a laminated sheet as set forth in any one of the Inventions 1-4.

[0013]

[Embodiment of the Invention]

The term laminated sheet" referred to in this invention means a product obtained by molding with heat and pressure from a plurality of prepreg sheets or with a metal foil clad product thereon. The term also includes multi-layered sheets comprising interior and surface layer printed wirings. The term repreg" in this invention means a single sheet obtained by impregnating a substrate such as a non-woven fabric or the like with a thermoset resin and drying, which is designed for subsequent use in above laminated sheet. The substrate for laminated sheet in this invention means a substrate for the above prepreg, namely a non-woven fabric or the like, before resin impregnation to form prepreg.

[0014]

The substrate for laminated sheets of this invention is a substrate for laminated sheets with a multi-layer structure having at least 3 layers. The substrate for laminated sheet of this invention has at least 3 layers so that this makes it possible to formulate layers having different physical properties between the 2 exterior layers and the internal layer so as to provide a substrate for laminated sheets with the characteristics of the respective layers. The properties for both exterior layers and the interior layer should be freely selected, depending upon the electronics application in which use is made.

[0015]

If one lets layer (A) represent the non-woven fabric used for the interior layer described in Claim 1, and layer (B) represent the non-woven fabric for the exterior layer, then the outermost layer should be layer (B) for the substrate of laminated sheet of this invention, without there being any restriction as to the number of layers (B). Similarly, it is required that there be a minimum of a single layer (A) other than the 2 exterior layers without being prevented from having a greater number of layers (A). For example, the invention may assume a construction B/A/A/B, B/B/A/B and the like. Incidentally, there is no need for the 2 exterior layers to be made of the same composition as long as they are within the scope described in Claim 1. Similarly, if there is more than 1 layer (A), there is no need for the all layers (A) to assume the same composition as long as they are within the scope described in Claim 1.

[0016]

Nonwoven fabrics which constitute the 2 exterior layers of this invention comprise a non-woven fabric containing at least 17% of a synthetic organic fiber having no melting point but having a decomposition temperature of at least 400°C with a content of synthetic organic fiber having a softening temperature not higher than 320°C being less than that of the interior layer. The term "softening temperature" in this invention is defined below. As the fiber is heated under a tensile stress using a TMA or the like, the fiber will soften near its melting point, beginning to flow, rapidly elongating until it breaks. The temperature at which the flow starts is called the softening temperature, which is lower than the melting point measured by DSC or the like (as is for Thermal Analysis" published by Kyoritsu Shuppan, 3rd edition, in 1996). This temperature can also be obtained from the tan δ, which may be derived by a dynamic viscoelastic measurement. The synthetic organic fiber used in the exterior layer non-woven fabrics preferably has the following configuration: a fiber diameter of 5-15μm and a fiber length of 1-6mm. A finer fiber diameter for the synthetic organic fiber would be more effective for increasing entanglement sites for the non-woven fabric, thus for strength of the wet papermade non-woven fabric, but the above range is generally selected for striking a balance between the factors of slurry dispersion and water filtration at the time of papermaking. While a longer fiber would be more effective for increasing the entanglement sites for fibers, thereby the strength of the wet papermade non-woven fabric, a shorter fiber length is preferred in terms of slurry dispersion during papermaking so that the above range is generally selected. Optionally, a binder is added to the non-woven fabric for the exterior layer. The binder, which can be added thereto, includes an aqueous soluble or emulsion resin or a hot bonding fibrous product. For the fibrous product it makes no difference whether it is a chopped strand or a fibrillated fiber. The binder type in terms of heat resistance is preferably a water soluble or emulsion type epoxy resin, acrylic resin, phenolic resin, or meta-aramid or polyarylate fibrous product, without being limited to them. The preferred binder type from the standpoint of heat resistance is an aqueous soluble or emulsion epoxy resin, acrylic resin, phenolic resin, or meta-aramid or polyarylate fibrous product without being limited to them. The non-woven fabrics for the exterior layer from the standpoint of minimizing the dirtying of tools for treatment with heat and pressure should

preferably contain at least 70% of a synthetic organic fiber having no melting point, but having a decomposition temperature of at least 400°C, more preferably a non-woven fabric consisting only of said fiber and a thermoset binder. The synthetic organic fibers having no melting point but having a decomposition temperature of at least 400°C to be used in the exterior layers are suitably p-phenylene terephthalamide fibers, p-phenylene diphenyl ether terephthalamide fibers, and poly-p-phenylene benzobisoxazole (PBO) fibers.

[0017]

The 2 exterior layers are required to be formulated with at least 70% of a synthetic organic fiber having a decomposition temperature of at least 400°C so that other fibers may be used in combination within the range of meeting the objective of the present invention. For example, a fiber having a softening temperature of not higher than 320°C may be formulated in the exterior layer, or a fiber having excellent properties in moisture absorption or dielectric constant may be formulated to achieve improvement in these properties. However, a fiber having a softening temperature not higher than 320°C should be formulated in a larger quantity in the interior layer from the standpoint of not dirtying the tools for treatment with heat and pressure, and the amount of the fiber having a softening temperature not higher than 320°C in the exterior layer should be formulated in an amount less than that in the interior layer in order to meet two requirements: reduction in dirtying the tools used for treatment with heat and pressure and improvement in the overall characteristics. The fiber having a softening temperature of not higher than 320°C to be used for the 2 exterior layers and the interior layer may be the same or different fibers. There may be cases when fibers having different levels of moisture absorption while having softening temperatures not higher than 320°C are used for the exterior and interior layers.

[0018]

The interior layer of this invention is constituted of a non-woven fabric comprising a synthetic organic fiber having a softening temperature of not higher than 320°C and a moisture absorption of not higher than 1.5%. From the standpoint of decreasing moisture absorption for the substrate for laminated sheets, it is suggested that the interior layer preferably contain such a fiber having a moisture absorption of not higher than 1.5%. Most of

such fibers today have melting points and softening temperatures of not higher than 320°C; the fact that such a fiber having a tendency to soften can be formulated in a large amount in the interior layer characterizes the present invention. Most of the low moisture absorption fibers today have melting points and softening temperatures of not higher than 320°C so that use of them in sufficient amounts has not been possible previously because formulating a large amount in order to minimize the moisture absorption of substrate for laminated sheets would cause a dirtying of the tools used for treatment with heat and pressure. The present invention, by virtue of formulating a large amount of such a fiber in the interior layer, enables the formation of a low moisture absorption substrate for laminated sheets without dirtying the tools used for a treatment with heat and pressure. The present invention makes it possible to incorporate a large amount overall of such a fiber that could not have been formulated in large amounts for the above reasons due to its having a melting point and the property of softening, even though it exhibits the useful properties as a substrate for laminated sheets, such as a low dielectric constant, furthermore, which incorporation provides a substrate for laminated sheets with excellent properties of not dirtying the tools used for treatment with heat and pressure. In order to take advantages of these features, it is preferred for the two exterior layers to contain a fiber having a softening temperature not higher than 320°C in an amount less than that for the interior layer. Incidentally, the term moisture absorption means the ratio of moisture absorption when moisture-conditioned at 20°C at 65% [relative humidity] for 24 hours; the specific dielectric constant here is the value measured at 1MHz. The configuration of the synthetic organic fiber used in the non-woven fabrics for the internal layer may be similar to one used in the exterior layer, which as in the case of external layer, may be mixed with an optional binder. The preferred binder material is similar to that for the exterior layer.

[0019]

The preferred synthetic organic fibers having a softening temperature of not higher than 320°C and a moisture absorption of not higher than 1.5% to be used in the interior layer of this invention from the standpoint of moisture absorption, are polyarylate fibers, polyphenylene sulfide fibers, and fluororesin fibers. Fluororesin fibers are preferred, not only for moisture absorption, but also for their low specific dielectric constant,

making them preferred from the standpoint of dielectric constant. It is particularly preferred for the content of the low moisture absorbing fiber to be formulated in an amount at least 30% in the interior layer so as to minimize the overall moisture absorption of the substrate for laminated sheets.

[0020]

The method for manufacturing substrate for laminated sheet in this invention is not particularly limited, but one of the preferred methods is to separately papermake non-woven fabrics by a wet papermaking method, followed by heating and drying, and overlaying the desired number of sheets on top of one another , and treating with heat and pressure using a pair of hot rolls at a surface temperature of 280°C-450°C, thereby softening the binder component contained in the sheet for bonding the fibers together. In order to generate resistance to warping in solder reflow steps or the like, the hot roll surface temperature is preferably higher, at least preferably 280°C or higher. A too high a hot roll surface temperature will cause tool dirtying and will degrade the fiber or the binder, causing a reduction in strength so that the temperature is preferably not higher than 450°C. If a treatment at a high temperature is needed, it is preferred to increase the content of the synthetic organic fiber having no melting point, but having a decomposition temperature of 400°C or higher, to be used in the 2 exterior layers. The treatment with heat and pressure by a hot roll calender may not be limited to just one time, but also may be 2 or more or several times.

[0021]

The substrate for the laminated sheet in this invention should have a density which is not particularly limited, and which can be suitably selected, depending upon the type of the resin used for impregnation in the manufacture of prepregs or applications, generally at levels 0.5-1.8g/m^3.

[0022]

The prepreg is prepared from the substrate for the laminated sheet of this invention by impregnation with a thermoset resin varnish, followed by heating and drying. The impregnating resin is in general, an epoxy resin, to which the invention is not limited; one may suitably select a resin normally

used in laminated sheets such as phenolic resin, polyimide resin, and the like.

[0023]

Laminated sheets from the prepregs of this invention can be prepared in the following manner: Copper foil is placed on both sides of a prepreg obtained by the present invention, followed by molding with heat and pressure, thereby, curing the resin which was in the semi-cured state in the prepreg, and cladding it with the copper foil , and further followed by producing a circuit pattern by the usual method and etching to form a circuit. It is also possible to obtain a so-called multi-layered sheet by pressing a plurality of prepregs overlaid one on top of one another . The method of pressing is not particularly limited, which can be suitably selected, depending upon the properties of the impregnating resins.

[0024]

[Examples]

The present invention is further specifically explained by the Examples of this invention below. Incidentally, the invention is not limited to the following examples.

[0025]

Raw materials used in the Examples of this invention and comparative examples are described below.

- Para-aramid fiber (Technora, moisture absorption: 2.0%, no melting point, decomposition temperature: at least 500°C, fiber diameter: 12μm, fiber length: 3mm, a product of Teijin)
- Para-aramid fiber (Kevlar 49, poly(p-phenylene terephthalamide), moisture absorption: 2.0%, no melting point, decomposition temperature: 630-650°C, a product of the DuPont Company)
- Poly-p-phenylene benzbisoxazole fiber (Zylon, no melting point, decomposition temperature: 560°C, a product of Toyobo),
- Polyarylate fiber (Vectran HS, Vectran NT, moisture absorption: 0.07%, melting point: 308°C, softening temperature: 257°C, fiber diameter 16μm, fiber length 6mm, both products of Kuraray Company)

• Polyphenylene Sulfide fiber (moisture absorption: 0.05%, melting point: 280°C, prepared by melt spinning, fiber diameter: 12μm, fiber length: 5mm),

• fluororesin fiber (moisture absorption: not more than 5%, melting point: 327°C;, produced by extruding PTFE resin by injection molding, fiber diameter: 12μm, fiber length: 3mm)

• Thermoset binder (aqueous epoxy resin, glass transition temperature: 110°C) was sprayed to give a wet sheet form, followed by heating and drying).

[0026] <Examples 1-12>

<Preparation of Substrates (Wet Preparation of Non-Woven Fabrics)>

Two non-woven fabrics for exterior layers and 1 sheet of non-woven fabric for internal layer, a total of 3 non-woven fabrics, were made into sheet by a wet papermaking method, in terms of the unit weights and formulations given in Table 1, followed by drying.

[0027]

<Preparation of Substrate (Bonding by Hot Rolls)>

The resultant non-woven fabrics were overlaid by interposing the interior layer between 2 exterior layer non-woven fabrics for a treatment with heat and pressure at the hot roll temperatures given in Table 1 to give the substrates for laminated sheeting having a metric unit weight of $72g/m^2$. The resultant substrates for laminated sheet could be treated with heat and pressure with no hot roll dirtying and had low moisture absorption.

[0028] <Comparative Examples 1-7>

Substrates for laminated sheets having a metric unit weight of $72g/m^2$ were obtained in a manner similar to that of Example 1, except for papermaking using formulations given in Table 2, followed by a treatment with heat and pressure using hot rolls at the temperatures given in Table 2. Incidentally, Comparative Examples 1,3,and 7 were all single layer structure substrates, otherwise the conditions for heat and pressure were identical to those of Example 1. Comparative Example 1 used the same formulation for the entire substrate as Example 1 (that is, the all materials for the exterior and interior layers for Example 1 were uniformly mixed to obtain a single layer, non-woven fabric); Comparative Example 3 had the same formulation as that of the exterior layers of Example 1. Comparative Example 2 having the

fiber (para-aramid fiber) with no melting point present in an amount not more than 70% for the exterior layers, showed much roll dirtying. Comparative Example 6, in which the roll temperature for treatment with heat and pressure was 450°C or higher, caused the paper to break at the roll site, making it impossible to continue the manufacturing.

[0029]

Laminated sheets were prepared by the method given below using substrates for laminated sheets obtained in the above Examples 1-12 and Comparative Examples 1-7, on which the following evaluations were made. The results are given in Tables 1 and 2.

<Measurement of Moisture Absorption>

A substrate for laminated sheets was impregnated with a brominated bisphenol A type epoxy resin varnish, followed by drying to obtain a prepreg with a resin pickup of 50%; 5 plies of it were overlaid one on top of each other, followed by placing an 18μm thick copper foil on both sides thereof, and subjected this assembly to molding for lamination with heat and pressure to give 0.5mm thick copper clad laminated sheet. The resultant laminated sheet was totally etched to remove the copper foil, left standing for 6 days under conditions of 60°C and 95% [RH]for moisture absorption, followed by drying to absolute dryness for 24 hours at 105°C to calculate the difference in weight. The difference in weight was divided by the weight of the absolutely dried laminated sheet and is reported as a moisture absorption and rated in the following 5 steps.

A 1 ≥ 0%, but less than 1.5%

B ≥ 1.50%, but less than 2.0%

C ≥ 2.0%, but less than 2.5%

D ≥ 2.5%, but less than 3.0%

E ≥ 3.0%, but less than 3.5%

<Warpage Measurement>

A laminate sheet prepared by the same method as used for measurement of moisture absorption was cut into a 400mm x 300mm size and totally etched to remove the copper foil, heated 1 hour at 230°C to measure any lifting at its 4 corners, which was averaged to be reported as warpage. Warpage was measured on the following examples to give the results as shown:

Example 4: 1.2mm
Example 12: 1.0mm
Comparative Example 5: 6.0mm

<Dielectric for Laminated Sheet>

A laminated sheet prepared by the same method used for laminated sheet and used for measurement of moisture absorption was totally etched to remove the copper foil, followed by treatment for absolute dryness for 24 hours at 105°C. Then the sample was moisture conditioned at a 20°C and 65% environment and subjected to a measurement for the specific dielectric constant using an RF Impedance/Material Analyzer 4291A of the Hewlett Packard Company at 1MHz. The dielectric constant for laminated sheets was measured on the following examples to obtain the results shown:

Example 11: 2.7
Comparative Example 7: 3.9

[0030]

[Table 1]

	Raw Material Composition	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8	Ex.9	Ex.10	Ex.11	Ex.12
Formation and Exterior Layers (%)	Para-aramid Fiber (Technora)	72			90	90	90	90	90	90	90	90	90
	PBO Fiber (Zylon)			90									
	Para-aramid Fiber (Kevlar 49)		90										
	Polyarylate Fiber Vectran (HS)	18											
	Fibrillated Meta-aramid Fiber (Nomex)					10							
	Fibrillated Polyarylate Fiber (Vectran MT)						10						
	Thermoset Resin Binder, Amount Added	10						10	10	10	10	10	10
	Metric Unit Weight of Exterior Layers	18	18	18	18	18	18	18	18	18	18	18	18
Interior Layer Formation (%)	Para-aramid Fiber (Technora)	62			30	30							
	PBO Fiber (Zylon)			30									
	Para-aramid Fiber (Kevlar 49)		30										
	Polyimide Fiber							60					
	Fluorofiber								60			90	
	Polyarylate Fiber (Vectran HS)	28	60	60	60	60	60				90		60
	Polyphenylene Sulfide									60			
	Fibrillated Meta-aramid Fiber (Nomex)					10							
	Fibrillated Polyarylate Fiber (Vectran MT)						10						
	Thermoset Resin Binder, Amount Added	10	10	10	10			10	10	10	10	10	10
	Metric Unit Weight of Interior Layer	36	36	36	36	36	36	36	36	36	36	36	36
Treatment with Heat and Pressure (g/m^2)		72.0	72.0	72.0	72.0	72.0	72.0	72.0	72.0	72.0	72.0	72.0	72.0
Hot Roll Temperature (°C)		320	320	320	320	320	320	320	320	320	320	320	340
Hot Roll Dirtying		O	O	O	O	O	O	O	O	O	O	O	O
Laminated Sheet Moisture Absorption (%)		B	B	A	B	B	A	B	B	B	A	A	B

[0031]

[Table 2]

	Raw Material Composition	Comp Ex.1	Comp Ex.2	Comp Ex.3	Comp Ex.4	Comp Ex.5	Comp Ex.6	Comp Ex.7
Formation	Para-aramid Fiber (Technora)		65		80	90	90	
and	PBO Fiber (Zylon)							
Exterior	Para-aramid Fiber (Kevlar 49)							
Layer (%)	Polyarylate Fiber (Vectran HS)		25		10			
	Fibrillated Meta-aramid Fiber (Nomex)							
	Fibrillated Polyarylate Fiber (Vectran MT)							
	Thermoset Resin Binder, Amount Added		10		10	10	10	
	Metric Unit Weight of Exterior Layer	0	18	0	18	18	18	0
Interior	Para-aramid Fiber (Technora)	68.5	80	72	85	30		90
Layer	PBO Fiber (Zylon)							
Formation	Para-aramid Fiber (Kevlar 49)							
(%)	Fluorofiber						60	
	Polyarylate Fiber (Vectran HS)	21.5	10	18	5	60	30	
	Polyphenylene Sulfide							
	Fibrillated Meta-aramid Fiber (Nomex)						30	
	Fibrillated Polyarylate Fiber (Vectran MT)						60	
	Thermoset Resin Binder, Amount Added	10	10	10	10	10	10	
								10
	Metric Unit Weight of Interior Layer	72	36	72	36	36	36	72
Treatment with Heat and Pressure (g/m^2)		72.0	72.0	72.0	72.0	72.0	72.0	72.0
Hot Roll Temperature (°C)		320	320	320	320	250	480	320
Hot Roll Dirtying		Much roll dirtying	Much roll dirtying	O	O	O	Paper break-down to make manufacturing impossible	O
Laminated Sheet Moisture Absorption (%)		C	C	D	E	A		F

[0032]

The Examples of this invention gave laminated sheets with low moisture absorption in every case, with less hot roll dirtying. Control examples had high moisture absorption except those samples which exhibited roll dirtying. A comparison of Example 11 with Comparative Example 7 shows that the substrate using a large amount of the fluororesin in an interior layer shows improvement in terms of hot roll dirtying and laminated sheet moisture absorption, in addition, it gives rise to a laminated sheet with a particularly low dielectric constant. In addition, a comparison of Example 12 with Comparative Example 5 shows that a laminated sheet from a substrate for laminated sheets treated with a heat pressure treatment hot roll at a temperature lower than 280°C provides good behavior in terms of hot roll dirtying and laminated sheet moisture absorption, but it suffers from substantial warpage.

[0033]

[Advantageous Effect of the Invention]

As described above, the present invention permits one to provide a substrate for laminated sheets and prepregs that can provide low moisture laminated sheets. It also provides a substrate for laminated sheets that can allow treatment with heat and pressure at sufficiently high temperature and a process for manufacture thereof. As a result, the invention was able to overcome the hot roll-dirtying problem. Furthermore, the present invention was able to provide a substrate for laminated sheets having excellent properties in terms of low dielectric constant and low warpage or the like.

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